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14. ABSTRACT

- Goal 1. Improved electrochemical test methods and protocols for characterizing the performance of coated aircraft alloys.
- Goal 2. Surface Analysis Studies of Degradation of Coatings Properties
- Goal 3. SVET Studies of Coated Aluminum Alloys
- Goal 4. Advanced Spectroscopy of Coating/Metal Systems
- Goal 5. Further examination of conductive polymers for chrome free metal pretreatment/ primers for Al alloys
- Goal 6. Development of molecular probes for examining changes in thin coating films during exposure
- Goal 7. Electrochemical Instrumentation Development
- Goal 8. Chrome-free pretreatment materials based on sol-gel optimization – new silicon oligomer design & synthesis
- Goal 9. Improved design/expert systems methods for total aircraft coatings systems design (with AFRL/ WPAFB).

Aircraft Corrosion, Environmentally Compliant Coatings

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Final Project Report
Executive Summary
September, 2002
For Grant F49620-99-0283
To: U.S. Air Force Office of Scientific Research
Program Manager: Lt. Colonel Paul Trulove

Corrosion Protection of Aluminum Alloys used in Aircraft - Testing, Analysis and Development
of Environmentally Compliant Coatings and Pretreatments for The Corrosion Protection of
Aircraft Alloys

From: North Dakota State University
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Prof. Dennis Tallman
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DISTRIBUTION STATEMENT A
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Part 1. Major Accomplishments

The details of our accomplishments during the past three years of research under this grant are easily assessable in journal articles and dissertations/theses (See Parts 2 and 3 for graduate's names and Journal titles, respectively). Additionally, detailed results have been presented in the annual reports which were prepared in September 2000, 2001, and 2002.

Goal I.

a.) **Electrochemical Characterization of Environmentally Compliant Aircraft Coatings Corrosion Protective Lifetimes and Continued Development of In-Situ Sensors for Corrosion**

Preliminary investigations used wavelet analysis of electrochemical noise data from intact coating systems on 2024 Al. The technique revealed no differentiation between poor and good coating data. The probable reason for this can be found in the literature; namely that wavelet analysis has limited application where data does not contain defined transient features in an otherwise random data set. Wavelet analysis is particularly useful in situations where transients are present and this has been borne out in the literature with studies of localized corrosion mechanisms such as pitting.

b.) **Examination of Wire-Beam Electrode Methods for Studies of Environmentally Compliant Aircraft Coatings based on both ENM and EIS**

The WBE was constructed and it is currently under development. It will be used as a reliable method to obtain a local value of the Noise Resistance of the coating systems. From the initial data, the WBE shows the potential to study electrochemical parameters locally over a metal surface and, consequently, to supplement the characterization of the systems that are actually performed with traditionally techniques.

c.) **Examination of Mg-rich Primer Coatings as a Cr-free Cathodic Protection Method for Al 2024 T-3**

The following conclusions can be reached based on this study:

1. The (Mg-rich primers + Extended Life Topcoat) coatings systems are the first non-chromated coatings systems to satisfy 3000 hours of such exposure and remain shiny and undamaged in the scribe area, only showing damage at about 4800 hours.
2. The degradation of Mg-rich coatings in acid-rain atmospheres was found to be controlled by the nature of the salts formed and was found not to be deleterious to the Al substrate.
3. A superior, room temperature cure, polymer matrix was synthesized by first reacting an amino-functional silane with an □□ unsaturated phenyl quinone. The silane modified imine/quinone serves as the

effective intermediate which can be incorporated into both the epoxy and urethane portions of the polymer's organic matrix.

4. Incorporation of a silane modified organic-inorganic Non-Covalent IPN with multi-functional crosslink potential yields a superior polymer system adding many desired properties including burn-flame resistance, adhesion, mechanical properties, total system performance, and durability.

Goal II

- a.) **Spectroscopy of Model Compounds**
- b.) **Atomic Force Microscopy of Model Compounds**
- c.) **Simulation of Degradation Processes**
- d.) **Internal Stress in Weathering Coatings**
- e.) **Utilize Scanning Kelvin Probe at AFRL/WPAFB**
- f.) **Incorporate Scanning Thermal Microscope into Durability studies**
- g.) **Porosity and Chromate Lifetime**

The most interesting aspect of the research so far is prediction of properties is functionally consistent with experimental results. These functional predictions are based on very general and simple assumptions of coating properties. The sigmoidal behavior of reflectance, for example, can be predicted by repeated application of random processes in conjunction with a simple model of how reflectance is affected by surface roughness

Goal III.

- a.) **Coatings Based on Derivatized ECPs.**

Various solvents have been investigated thus far in the electropolymerization studies of the 3-alkylaminothiophenes, each with varying results and properties. Currently, a dialkylaminothiophene is being studied. Removing the hydrogen and replacing it with an additional alkyl group can hopefully avoid the problems caused by the hydrogen bonding. Preliminary data collection using this new monomer show promising results. Future work will now be conducted using this monomer versus the one previously discussed.

Corrosion protection abilities of polyaniline in the EB and NaSPAN form had been evaluated and investigated by scanning vibrating electrode technique on Al 2024-T3 alloy. It was exhibited that both of the two forms of polyaniline were promising corrosion protection coatings to replace chromate-containing coating.

The SVET results of the EB and NaSPAN polyaniline coated Al 2024-T3 exhibited similar electrochemical activity, which was oxidation/reduction current occurring within the defect area. The fact was also similar to that happened on chromated-epoxy coated Al 2024-T3. The NaSPAN provide better corrosion protection to the defect area than EB or chromated-epoxy coating. The corrosion delay time of NaSPAN coated sample (13 hours) was much longer than that of EB

(typically 3.5 hours) and chromated-epoxy coating (5.5 hours). The fact was explained as that NaSPAN may have stronger throwing power to dissolve away the copper-containing product from the surface of the corroding aluminum alloy, which eliminated the presence of a galvanic couple between Aluminum and copper. The effect significantly reduced the corrosion rate.

It is suggested that there were at least two possible mechanisms behind the corrosion inhibition of the polypyrrole. Case 1: perhaps the dopant can act as a corrosion inhibitor. Case 2: perhaps the redox behavior of the polymer determines the interaction of the ECP with the metal substrate.

b.) Direct Electrodeposition of ECPs.

We recently reported a new approach for directly depositing electroactive conducting polymers (ECPs) onto aluminum and aluminum alloy Al 2024-T3. The method involves using an electron transfer mediator (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt, or Tiron[®]) which reduces the deposition potential of polypyrrole by nearly 500 mV and results in uniform, adherent, conducting, electroactive films. The lower deposition potential avoids oxidation of the aluminum substrate and polymer formation occurs with nearly 100% current efficiency.

We have now examined this mediated deposition process over a wider range of conditions, including monomer concentration, mediator concentration, pH, and charge density. Corrosion studies of electrodeposited polypyrrole on Al 2024-T3 with a polyurethane topcoat have been underway for nearly a year. Samples in both immersion and Prohesion[™] have shown good corrosion resistance during this period. Results will be reported in due course.

Additionally, we have looked at finding different chemical oxidants, which would serve the purpose of initializing the deposition process. Ideally, the oxidant would cause polymerization, forming a uniform coating of polypyrrole in a reasonable amount of time and provide good corrosion inhibition properties.

Goal IV.

- a.) Blending functionalized polysiloxanes with organic resins**
- b.) Synthesize a variety of functionalized polysiloxanes**

- Successful Construction of Cohesive Coating System by Chemically Tailored Aluminum Surface
- Aluminum / Primer / Topcoat Adhesion ~ 1000 psi
- Moderate Corrosion Protection
- Demonstrated Ability to Modify Primer Properties
 - Changing Functionalities

- Polymer Blending Capability
- Successful Cohesive Coating System
- Corrosion Protection Improvement

Part 2. Personnel Contributing to this Study

Year 1

Lingyun He (Graduate Student – 100%), M. Nanna (Graduate Student - 100%), Gordon Bierwagen (PI – 7%)

X.F.Yang (Post-Doctoral Associate – 30%), C. Vang (Graduate Student - 50%), V. Johnston-Gelling (Graduate Student - 100%), D.E.Tallman (co-PI - 20 %), J. Hie (Graduate Student - 100%), Thane Underdahl (Graduate Student - 25%), G.P.Bierwagen (PI-2%), M. Wiest (Undergraduate 10 %), and S.Rohlik (Undergraduate 10 %)

Dr. Thomas Ready (Post-Doctoral Associate – 100%), Dr. Bhanu P.S. Chauhan (Post-Doctoral Associate – 75%), Dr. Moni Chauhan (Post-Doctoral Associate – 25%), Dr. Seok-Bong Choi (Post-Doctoral Associate – 10%), P. Boudjouk (co-PI - 5%)

Mukund Sibi (Co-PI – 2%)

Gerardo Miramontes de Leon (Graduate Student - 82%), Debashis Banerjee (Graduate Student - 78%), Jyotirmy Datta (Graduate Student - 67%), David C. Farden (co-PI - 12%)

Year 2

Lingyun He (Graduate Student – 100%), Gordon Bierwagen (PI – 5%), Stephen Mabbutt (Post-Doctoral Associate-100%) M. Nanna (Graduate Student – 100 %), Junping Li (Graduate Student – 100 %), (Lisa Ellingson (Graduate Student – 50%), Xianping Wang (Graduate Student – 100 %), Dante Battocchi (Graduate Student – 100 %), Jonathan Wegner (Undergraduate student -10%), Tom Hrdlicka (Undergraduate student -10%), Ryan Bennett (Undergraduate 10 %), Kristopher Spenningsby (Undergraduate 10 %) and S.Rohlik (Undergraduate 10 %)

S. G. Croll (PI - 15%), A. D. Skaja - graduate student (50%) C. Vang (Graduate Student - 50%), X.F.Yang (Post-Doctoral Associate – 50%)

D.E.Tallman (PI - 20 %), C. Vang (Graduate Student - 50%), X.F.Yang (Post-Doctoral Associate – 50%), V. Johnston-Gelling (Graduate Student - 100%), J. Hie (Graduate Student - 100%), Thane Underdahl (Graduate Student - 25%), G.P.Bierwagen (PI-2%), M. Wiest (Undergraduate 10 %), M. Dewald (Undergraduate student -10%), and A. Richter (Undergraduate student -10%)

Postdoctoral Research Associates - Dr. Thomas Ready, 100%, - Dr. Seok-Bong Choi, 100%

David C. Farden, Co-PI, 18%, Debashis Banerjee, (Graduate Student-100%), Jyotirmy Datta (Graduate Student-100%), Md. Jafarullah (Graduate Student-100%)

Mukund Sibi (Co-PI – 2%), Zhengang Zong (Post-doctoral Associate-100%)

NOTE: *Three students working on this program earned graduate degrees from NDSU during the year.*

Lisa Ellingson received her MS in Polymers & Coatings Science

Debashis Banerjee received his MS in Electrical and Computer Engineering

Junping Li received his PhD in Polymers & Coatings Science.

Year 3

Goal I.

Lingyun He (Graduate Student – 100%), Gordon Bierwagen (PI – 5%), Stephen Mabbutt (Post-Doctoral Associate-100%) M. Nanna (Graduate Student – 100 %), Xianping Wang (Graduate Student – 100 %), Dante Battocchi (Graduate Student – 100 %), Jonathan Wegner (Undergraduate student -10%), Tom Hrdlicka (Undergraduate student -10%), Ryan Bennett (Undergraduate 10%), Kristopher Spenningsby (Undergraduate 10 %), and Anthony Stamness(graduation 50%)

Goal II

S. G. Croll (PI - 15%), A. D. Skaja - graduate student (90%), B. Hinderliter – Postdoctoral Research (100%), D. Fernando – graduate student (100%), L. Jensen – visiting summer undergraduate researcher (100%)

Goal III

D. E. Tallman (PI - 20 %), C. Vang (Graduate Student - 80%), X. F. Yang (Post-Doctoral Associate - 50%), V. Johnston Gelling (Graduate Student - 50%), J. Hie (Graduate Student - 100%), J. Stafford (Graduate Student - 100%), M. Dewald (Graduate Student -50%), T. Underdahl (Graduate Student - 100%), G. P. Bierwagen (PI - 2%), and A. Richter (Undergraduate student - 30%)

Goal IV

Postdocotoral Research Associates - Dr. Thomas Ready, 100%, - Dr. Seok-Bong Choi, 100%

NOTE: *One student working on this program earned a graduate degree from NDSU during the year.*

Victoria Johnston Gelling earned her Ph.D. from the Chemistry Department.

Three more students (Jie He, Lingyun He, and Chur Vang) L will defend their Ph.D.s within the next few months.

Part 3. Publications

Journal Article Publications

Year 1

J. He, V. Johnston-Gelling, D.E. Tallman, and G.P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated Epoxy Primer on Steel and Aluminum," J. Electrochem. Soc. (2000) in press.

J. He, V. Johnston-Gelling, D.E. Tallman, G.P. Bierwagen, and G.G. Wallace, "Conducting Polymers and Corrosion 3: A Scanning Vibrating Electrode Study of Poly(3-Octyl Pyrrole) on Steel and Aluminum," J. Electrochem. Soc. (2000) in press.

V.J. Gelling, M.M. Wiest, D.E. Tallman, G.P. Bierwagen and G.G. Wallace, "Electroactive Conducting Polymers for Corrosion Control: Studies of Poly(3-Octyl Pyrrole) and Poly(3-Octadecyl Pyrrole) on Aluminum 2024-T3 Alloy," Prog. Organic Coatings (2000) accepted.

"New Neutral Carrier-type Ion Sensors. Crown Ether Derivatives of Poly(methylhydro siloxane)", B. P. S. Chauhan and P. Boudjouk, Tetrahedron Lett., 40, 4123-4126, 1999.

"A New Catalyst for Exclusive β -Hydrosilylation of Acrylonitrile", M. Chauhan and P. Boudjouk, Tetrahedron Lett., 40, 4127-4128, 1999.

"New Organosilicon Polymer for the Extraction and Phosphorescence Analysis of Uranyl in Environmental Samples", A. F. Arruda, A. D. Campiglia, B. P. S. Chauhan, and P. Boudjouk, Anal. Chim. Acta, 396, 263-272, 1999.

"An Efficient Pd-Catalyzed Route to Silyl Esters" M. Chauhan, B. P. S. Chauhan and P. Boudjouk, Org. Lett., 2, 1027-1029, 2000.

"Dehydrogenative Condensation of SiH and SH Bonds. A Metal-catalyzed Protocol to Stable Thiopolysiloxanes" B. P. S. Chauhan, P. Boudjouk, Tetrahedron Lett., 41, 1127-30, 2000.

"Facile and Efficient Synthesis of Siloxane Based Polyamines", T. E. Ready, B. P. S. Chauhan and P. Boudjouk, Macromolecules, Macromolecular Rapid Commun., in press

"A Catalytic Route to Grafted Silicones", B. P. S. Chauhan, T. E. Ready, Z. Al-Badri and P. Boudjouk, Organometallics, in press.

Year 2

Gordon P. Bierwagen, Dennis E. Tallman, "Choice and Measurement of Crucial Aerospace Coating System Properties," Prog. Organic Coatings, 41 (2001) 201-217

Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," Proceeding of the XXVth FATIPEC Congress, Turin, Italy, September 19-23, 2000, Vol. I, pp. 1-21, also as: Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," J. Coatings Tech., 73(#915) (2001) 45.

Gordon P. Bierwagen*, J. Li, L. He & L. Ellingson & D.E. Tallman, "Consideration of a New Accelerated Evaluation Method for Coating Corrosion Resistance – Thermal Cycling Testing," Prog. Organic Coatings, 39 (2000) 67-78

R.L. De Rosa, J.T. Grant, L. Kasten, M. Donley, & G.P. Bierwagen, "Surface Analysis of Various Methods of Preparing Al 2024 T-3 Surface for Painting," Corrosion, 56 (2000) 395-400

G. Miramontes de Leon, D.C. Farden, and D.E. Tallman, "Transient Analysis and Simulation of Pitting Corrosion for the Estimation of the Noise Resistance," Corrosion, 56, pp. 928-934, September 2000.

J. He, V. Johnston-Gelling, D.E. Tallman and G.P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated-Epoxy Coatings on Steel and Aluminum," *Polymer Preprints*, 41 (2000) 1755-1756.

J. He, V. Johnston-Gelling, D.E. Tallman and G.P. Bierwagen, "Scanning Vibrating Electrode Study of Electronically Conducting Polymers on Aluminum Alloy," *Polymer Preprints*, 41 (2000) 1774-1775.

V. Johnston-Gelling, D.E. Tallman, G.P. Bierwagen and G.G. Wallace, "Study of Poly(3-Octyl Pyrrole) for Corrosion Control of Aluminum 2024-T3," *Polymer Preprints*, 41 (2000) 1770-1771.

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X.F. Yang, D.E. Tallman, V. Johnston, G.P. Bierwagen, and J. Berg, "Use of Sol-gel Conversion Coating for Aluminum Corrosion Protection", *Surface & Coatings Technology* (2001) in press.

V. Johnston-Gelling, M.M. Wiest, D.E. Tallman, G.P. Bierwagen and G.G. Wallace, "Electroactive Conducting Polymers for Corrosion Control: Studies of Poly(3-Octyl Pyrrole) and Poly(3-Octadecyl Pyrrole) on Aluminum 2024-T3 Alloy," *Prog. Organic Coatings* (2001) in press.

D.E. Tallman, G.M. Spinks, A.J. Dominis, and G.G. Wallace, "Electroactive Conducting Polymers for Corrosion Control. Part 1. General Introduction and a Review of Non-Ferrous Metals," *J. Solid State Electrochem.* (2001) in press.

G.M. Spinks, A.J. Dominis, G.G. Wallace and D.E. Tallman, "Electroactive Conducting Polymers for Corrosion Control. Part 2. Ferrous Metals," *J. Solid State Electrochem.* (2001) in press.

X.F. Yang, C. Vang, D.E. Tallman, G.P. Bierwagen, S.G. Croll, S. Rohlik, "Weathering Degradation of the Polyurethane Coating," *Polymer Degradation and Stability* (2001) to be submitted.

G. Teng, M.D. Soucek, X.F. Yang and D.E. Tallman, "Effect of Addition Mode of Cycloaliphatic Diepoxide on Morphology and Film Properties of Crosslinkable Core-Shell Latex," *Journal of Applied Polymer Science* (2001) submitted.

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M. Chauhan, B. P. S. Chauhan and P. Boudjouk, "An Efficient Pd-Catalyzed Route to Silyl Esters" *Org. Lett.* 2000, 2, 1027-1029.

B. P. S. Chauhan, P. Boudjouk, "Dehydrogenative Condensation of SiH and SH Bonds. A Metal-catalyzed Protocol to Stable Thiopolysiloxanes," *Tetrahedron Lett.*, 2000, 41, 1127-30.

T. E. Ready, B. P. S. Chauhan and P. Boudjouk, "Facile and Efficient Synthesis of Siloxane Based Polyamines", *Macromolecular Rapid Commun.*, 2001, 22, 654-657.

B. P. S. Chauhan, T. E. Ready, Z. Al-Badri and P. Boudjouk, "A Catalytic Route to Grafted Silicones", *Organometallics* 2001, 20,

M.P. Sibi & Z.Zhong, "Determination of Corrosion on Aluminum Alloy under Protective Coatings using Fluorescent Probes," submitted to *Prog. Organic Coatings*

Year 3

R.L. De Rosa, D.A. Earl, G.P. Bierwagen, "Statistical evaluation of EIS and ENM data collected for monitoring corrosion barrier properties of organic coatings on Al-2024-T3," *Corrosion Science*, 44 (2002) 1607-1620

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G. M. Spinks, A. J. Dominis, G. G. Wallace and D. E. Tallman, "Electroactive Conducting Polymers for Corrosion Control. Part 2. Ferrous Metals," *J. Solid State Electrochem.* 6 (2002) 85-100.

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C. Vang, M. Dewald, A. Richter, D. E. Tallman, G. G. Wallace and G. P. Bierwagen, "Electrocatalytic Polymerization of Polypyrrole on Al 2024-T3 Alloy," *Polymer Preprints* 43 (2002) 742-743.

C. Vang, M. Dewald, J. He, A. Richter, D. E. Tallman, and G. P. Bierwagen, "Conductive Polymer Blend Composites for Corrosion Inhibition," *Polymer Preprints* 43 (2002) 401-402.

X. F. Yang, D. E. Tallman, G. P. Bierwagen, S. G. Croll, S. Rohlik, "Blistering and Degradation of Polyurethane Coatings under Different Accelerated Weathering Tests," *Polymer Degradation and Stability* 77 (2002) 103-109.

X. F. Yang, D. E. Tallman, S. G. Croll and G. P. Bierwagen, "Electrodeposition of Polypyrrole on Aluminum Alloy. Effect of Surface Preparation," *Proceedings of the International Conference on Surface Modification Technologies* 15 (2002) 119-126.

G. Teng, M. D. Soucek, X. F. Yang and D. E. Tallman, "Effect of Addition Mode of Cycloaliphatic Diepoxide on Morphology and Film Properties of Crosslinkable Core-Shell Latex," *Journal of Applied Polymer Science* (2002) in press.

X. F. Yang, D. E. Tallman, G. P. Bierwagen, S. G. Croll, L. S. Kasten, S. Rohlik "Hydrolytic Degradation of Polyurethane Coatings," *Polymer Degradation and Stability* (2002) in press.

S. G. Croll and A. D. Skaja, "Quantitative Use of Ultraviolet Spectroscopy To Calculate the Effective Irradiation Dosage During Weathering," *Macromolecular Symposia, XXVI FATIPEC Congress, "Coatings and Pigments,"* September 9 - 11, 2002. Wiley-VCH, Weinheim Germany.

S. G. Croll and A. D. Skaja, "Quantitative Ultraviolet Spectroscopy in Weathering of a Model Polyester-Urethane Coating," Accepted in *Polymer Degradation and Stability*.

S. G. Croll and A. D. Skaja, "Spectroscopic Adsorption And Effective Dosage in Accelerated Weathering of a Polyester-Urethane Coating," *J. Mats. Sci.* In Press

D. E. Tallman, C. K. Vang, M. P. Dewald, G. G. Wallace, G. P. Bierwagen, "Electron Transfer Mediated Deposition of Conducting Polymers on Active Metals," *Synthetic Metals* (2002) submitted.

G. P. Bierwagen, J. Li, L. He, L. Ellingson, and D. E. Tallman, "Consideration of a New Accelerated Evaluation Method for Coating Corrosion Resistance – Thermal Cycling Testing," *Prog. Organic Coatings* (2002) submitted.

Chemical Degradation of a Self-Priming (Unicoat) Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: I. An FTIR Spectroscopy Approach. Submitted to Polymer Degradation and Stability

Chemical Degradation of a High Gloss Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: II. An FTIR Spectroscopy Approach. Submitted to Polymer Degradation and Stability

Chemical Degradation of a Fluorinated Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: III. An FTIR Spectroscopy Approach. Submitted to Polymer Degradation and Stability

Lingyun He, Gordon. P. Bierwagen and Dennis. E. Tallman, "Use of a Scanning Thermal Microscope to Examine Corrosion Protective Coatings in Exposure," Submitted to Progress in Organic Coatings, from Keystone II WORKSHOP ON NANOSCALE APPROACHES TO MULTIFUNCTIONAL COATINGS, August 2002.

Gordon Bierwagen, Tara J. Shedlosky, Kimberly Stanek, "Developing and Testing a New Generation of Protective Coatings for Outdoor Bronze Sculpture," Submitted to Progress in Organic Coatings, from Athens 2002 Int. Conference on Organic Coatings Science, July 2002, Athens Greece.

Gordon Bierwagen, Dennis Tallman*, Junping Li and Lingyun He, "EIS Studies of Coated Metals in Accelerated Exposure," Submitted to Progress in Organic Coatings, from 5th International Symposium on Electrochemical Impedance Spectroscopy EIS 2001, Marilleva, Italy June 2001.

G.P.Bierwagen, X. Wang, & D.E. Tallman, "The *In-Situ* Study of Coatings Using Embedded Electrodes for ENM Measurements," Submitted to Progress in Organic Coatings, from International Workshop: Application of Electrochemical Techniques to Organic Coatings, Jurata, Poland May 2001.

Refereed Book/Proceedings Chapters

Gordon Bierwagen, Junping Li, Lingyun He, and Dennis E. Tallman "Fundamentals of the Measurement of Corrosion Protection and the Prediction of Its Lifetime in Coatings," Chapter 16 in *Proceedings of the 2nd International Symposium on Service Life Prediction Methodology and Metrologies*, Monterey, CA, Nov. 14-17, 1999, ACS Symposium Series # 805, J. Martin and D Bauer, ed., ACS Books, Washington, DC (2002) 316-350

Dennis E. Tallman, Jie He, Victoria Johnston Gelling, Gordon P. Bierwagen, and Gordon G. Wallace, "Scanning Vibrating Electrode Studies of Electroactive Conducting Polymers on Active Metals," ACS Books, Washington, DC (2002) in press.

Gordon G. Wallace, Anton Dominis, Geoffrey M. Spinks and Dennis E. Tallman, "Factors Influencing the Performance of Inherently Conducting Polymers as Corrosion Inhibitors - The Dopant," ACS Books, Washington, DC (2002) in press.

Part 4. Interactions/Transitions

Year 1

"Studies of Inherently Conducting Polymers for Corrosion Inhibition of Aluminum and Steel," with V. Johnston-Gelling, J. He and G. P. Bierwagen, 14th International Corrosion Congress, September 26-October 1, 1999, Cape Town, South Africa.

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," The University of Wollongong, November 23, 1999, Wollongong, NSW, Australia, **Invited Lecture**.

"Application of the Scanning Vibrating Electrode Technique for Probing Interactions between Conductive Electroactive Polymers and Active Metals," with Victoria Johnston Gelling, Jie He, Gordon P. Bierwagen, and Gordon G. Wallace, 11th Royal Australian Chemistry Institute Conference (RACIC), February 6-11, 2000, Canberra, ACT, Australia, **Invited Presentation**.

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," Commonwealth Scientific and Industrial Research Organization (CSIRO), March 30, 2000, Melbourne, Australia, **Invited Lecture**.

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," Joint North Dakota, South Dakota and Minnesota Academy of Sciences Meeting, Symposium on "Electrochemistry and Characterization of Complex Surfaces," April 28, 2000, Moorhead, Mn, **Invited Presentation**.

"Electroactive Conducting Polymer Coatings for Corrosion Protection," 32nd American Chemical Society Great Lakes Regional Meeting, Symposium on "Coatings Materials for the 21st Century," June 4-7, 2000, Fargo, ND, **Invited Presentation** (symposium co-organizer).

"Electroactive Conducting Polymers for Corrosion Control: Studies of Poly(3-Octyl Pyrrole) and Poly(3-octadecyl pyrrole) on Aluminum 2024-T3 Alloy," with Victoria Johnston Gelling, Michelle Wiest, Gordon P. Bierwagen and Gordon G. Wallace, 26th Annual Conference on Organic Coatings, July 3-7, 2000, Athens, Greece, **Invited Presentation**.

"Scanning Vibrating Electrode Studies of Electronically Conducting Polymers on Aluminum Alloy," with Jie He, Victoria Johnston Gelling and Gordon P. Bierwagen, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, **Invited Presentation**.

"Study of Poly(3-Octyl Pyrrole) for Corrosion Control of Aluminum 2024-T3," with Victoria Johnston Gelling, Gordon P. Bierwagen and Gordon G. Wallace, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

"A Scanning Vibrating Electrode Study of Chromated-Epoxy Coatings on Steel and Aluminum," with Jie He, Victoria Johnston Gelling and Gordon P. Bierwagen, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

33rd Organosilicon Symposium, Midland MI, April 6-8, 2000; Poster #12
"A Facile and Efficient Route to Polysilyl Esters", M. Chauhan, B. P. S. Chauhan, and P. Boudjouk

33rd Organosilicon Symposium, Midland MI, April 6-8, 2000; Poster #13
"A 'One-Pot' Route to Grafted Hybrid Silicones", B. P. S. Chauhan, and P. Boudjouk

33rd Organosilicon Symposium, Midland MI, April 6-8, 2000; Poster #14
"Functionalized Polysiloxanes as Primer Components in Coating Systems", T. E. Ready, P. Boudjouk, S. Rohlik, V. Gelling, D. E. Tallman and G. Bierwagen

32nd Great Lakes Regional Meeting of the American Chemical Society, Fargo, ND; June 4-6, 2000
"A One Pot Catalytic Approach to Silicone Co-Polymers", B. P. S. Chauhan, and P. Boudjouk

32nd Great Lakes Regional Meeting of the American Chemical Society, Fargo, ND; June 4-6, 2000
"Synthesis, Characterization and Morphological Investigations of Multimetallic Silicones", Z. Al-Badri, B. P. S. Chauhan, and P. Boudjouk.

Year 2

a. Presentations

Gordon Bierwagen, "EIS Studies of Coated Metal in Accelerated Exposure," **Invited Keynote Speaker**, EIS 2001, Marilleva-Trento, Italy, June 17-22, 2001

Gordon Bierwagen, "Chromate-Free Corrosion Protective Coatings Systems for Al Alloy 2024-T3," **Invited Lecture** at Aluminum Chair 2001 – Aluminum in the Aerospace Industries, Gosselies, Belgium, March 22, 2001

Gordon Bierwagen, "Past and Present Development of the CPVC Concept and Its Applications to Coatings Design and Formulation," **Invited Presentation** to the Philadelphia Society for Coatings Technology, March 1, 2001

Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," **Invited Plenary Lead-Off Lecture**, XXVth FATIPEC 2000 Congress, Turin, Italy, September 19-23, 2000

Philip Boudjouk, **Invited Presentation**, "Modifying Silicon-Carbon Structures as Sol-Gel Precursors or Monomers for Protective Polymers," 2001 Athens Conference on Organic Coatings Science and Technology, Athens Greece, July 6, 2001

D.E.Tallman, "Scanning Vibrating Electrode Studies of Electronically Conducting Polymers on Aluminum Alloy," with Jie He, Victoria Johnston Gelling and Gordon P. Bierwagen, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, **Invited Presentation**.

D.E.Tallman, "Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Nankai University, October 9, 2000, Tianjin, China, **Two Invited Lectures**.

D.E.Tallman, "Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Shandong Normal University, October 13, 2000, Jinan, China, **Two Invited Lectures**.

D.E.Tallman, "Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," North China Institute of Technology, October 16, 2000, Taiyuan, China, **Two Invited Lectures**.

D.E.Tallman, "Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Central Iron and Steel Research Institute, October 19, 2000, Beijing, China, **Two Invited Lectures**.

S.G.Croll, "Durability Studies of Urethane Aircraft Coatings using Quantitative Spectroscopy and Atomic Force Microscopy," poster presentation with Allen D. Skaja & Xiaofan F. Yang Gordon Research Conference on Coatings and Films, Colby-Sawyer College, July 2001

Gordon Bierwagen, Xianping Wang, & Dennis Tallman, "Embedded Electrodes for *In Situ* ENM Measurements," Presented at The Second International Workshop "Application of Electrochemical Techniques to Organic Coatings," Jurata, Poland, May 14-17, 2001

Gordon Bierwagen, Xianping Wang, & Dennis Tallman, "Use of Electrochemical Noise Methods (ENM) for *In Situ* Monitoring of Coatings Electrochemical Properties During Accelerated Exposure Testing," Paper 178 Presented at the 199th Meeting of The Electrochemical Society, Washington, DC, March 25-30, 2001

M. Abbas and D. C. Farden, "1-D FIR Filter Design by Smoothing the Transition Band Using the Cosine Roll-Off," ICIMADE 2001, June 2001, Fargo ND. "Direct Electrodeposition of Polypyrrole on Al 2024-T3 by Electron Transfer Mediation," with C. Vang, A. Richter, G. G. Wallace and G. P. Bierwagen, 200th Meeting of the Electrochemical Society, September 2-7, 2001, San Francisco, CA, poster presentation.

Victoria Johnston Gelling, Dennis Tallman, Gordon P. Bierwagen and Gordon G. Wallace, "Study of Poly(3-Octyl Pyrrole) for Corrosion Control of Aluminum 2024-T3," 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

Jie He, Dennis Tallman, Victoria Johnston Gelling and Gordon P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated-Epoxy Coatings on Steel and Aluminum," 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

J. Li & L. He, X. Yang and V. Gelling and Z. Zong made poster presentations at the AFOSR January 2001 Review, Hawk's Cay, FL.

Year 3

a. Presentations

"Direct Electrodeposition of Polypyrrole on Al 2024-T3 by Electron Transfer Mediation," C. Vang, A. Richter, D. E. Tallman, G. G. Wallace and G. P. Bierwagen, 200th Meeting of the Electrochemical Society, September 2-7, 2001, San Francisco, CA, poster presentation.

"Corrosion Studies of Electrodeposited Polypyrrole Coatings on Al 2024-T3 Alloy," C. Vang, J. He, A. Richter, D. E. Tallman, G. G. Wallace and G. P. Bierwagen, 200th Meeting of the Electrochemical Society, September 2-7, 2001, San Francisco, CA, poster presentation.

"Deposition of Conjugated Electroactive Polymers on Active Metals by Electron Transfer Mediation," D. E. Tallman, University of Northern Iowa, November 1, 2001, Cedar Falls, IA.

"Corrosion Research at North Dakota State University," D. E. Tallman, University of Cincinnati, November 26, 2001, Cincinnati, OH.

"The Scanning Vibrating Electrode Technique for Corrosion Studies," D. E. Tallman, Workshop on Scanning Probe Techniques, The University of Wollongong, December 17, 2001, Wollongong, NSW, Australia, **Invited Lecture**.

"Direct Electrodeposition of Polypyrrole on Al 2024-T3 by Electron Transfer Mediation," D. E. Tallman, The University of Wollongong, December 20, 2001, Wollongong, NSW, Australia, **Invited Lecture**.

"Deposition of Conjugated Electroactive Conducting Polymers on Active Metals by Electron Transfer Mediation," D. E. Tallman, Academia Sinica, December 25, 2001, Taipei, Taiwan, **Invited Lecture**.

"Electrodeposition of Conducting Polymer Coatings on Active Metals using Electron Transfer Mediation," D. E. Tallman, C. Vang, T. Underdahl, G. G. Wallace, and G. P. Bierwagen, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, **Invited Presentation**.

"The Study of Polypyrrole as a Corrosion Inhibitor of Aluminum Alloy 2024-T3," V. Johnston Gelling, D. E. Tallman, G. P. Bierwagen and G. G. Wallace, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, Poster Presentation.

"Investigation and Evaluation of the Performance of Aircraft Coatings under QUV/Prohesion Alternating Exposure," X. F. Yang, J. Li, D. E. Tallman, S. G. Croll, G. P. Bierwagen and J. T. Grant, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, Poster Presentation.

"Aircraft Coatings Testing, Corrosion Sensors in Coatings and Mg-Rich Coatings as Cr-Free Primers for Al 2024-T3," G. P. Bierwagen, S. Mabbutt, L. He, X. Wang, M. Nanna, L. Ellingson and D. E. Tallman, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, Oral Presentation.

"Aircraft Coatings Protective Lifetime Testing," S. Mabbutt, J. Li, J. Wegner, G. P. Bierwagen and D. E. Tallman, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, Poster Presentation.

"Coating Performance Evaluation Protocol using Electrochemical and Physical Methods," S. J. Mabbutt, J. Li, G. P. Bierwagen and D. E. Tallman, 2002 Tri-Service Corrosion Conference, January 14-18, 2002, San Antonio, TX, Poster Presentation.

"Direct Electrodeposition of Polypyrrole on Aluminum and Aluminum Alloy by Electron Transfer Mediation," D. E. Tallman, C. Vang, G. G. Wallace and G. P. Bierwagen, The Pittsburgh Conference, March 17-22, 2002, New Orleans, LA, Oral Presentation.

"Electron Transfer Mediated Deposition of Conducting Polymers on Active Metals," D. E. Tallman, C. Vang, M. Dewald, G. G. Wallace and G. P. Bierwagen, International Conference on Science and Technology of Synthetic Metals, June 29-July 4, 2002, Shanghai, China, Oral Presentation.

Stuart Croll presented at American Chemical Society, American Physical Society, European Physical Society, Ford Motor Company, and Keystone.

Gordon Bierwagen, Xianping Wang, and Dennis Tallman "In-Situ ENM and EIS Measurements by the Use of Imbedded Electrodes in Coating Films," presented at 5th International Aircraft Corrosion Workshop to 20-23 August 2002, NAVAIR, Solomons, MD**

Lingyun He, Gordon. P. Bierwagen and Dennis. E. Tallman, "Use of a Scanning Thermal Microscope to Examine Corrosion Protective Coatings in Exposure," Paper presented at Keystone II WORKSHOP ON NANOSCALE APPROACHES TO MULTIFUNCTIONAL COATINGS, Keystone, CO August 2002.

S.J. Mabbutt* & G. P. Bierwagen "Electrochemical Noise Methods to Investigate Anti-Corrosive Coatings," Submitted Presentation at *Rust 2002*, Us Navy & Industry Corrosion Technology Exchange, Louisville, KY July 8-11, 2002.

Gordon Bierwagen Tara J. Shedlosky*, and Kimberly Stanek, "Developing and Testing a New Generation of Protective Coatings for Outdoor Bronze Sculpture," Invited Presentation at the 28th Athens international Conference on Organic Coatings Science, Athens (Vouliagmeni), Greece, July 4, 2002.

Gordon Bierwagen, "The Use of Electrochemical Noise Methods (ENM) to Study Coated Metals," Invited Lecture at the University of Trento, Trento, Italy March 19, 2002

Gordon Bierwagen, "Assessment of the Corrosion Protective Lifetimes of Organic Coatings," Invited Presentation at Ford Motor Co., Scientific Laboratories, Dearborn, MI March 12, 2002.

G. P. Bierwagen, S. Mabbutt, X. Wang, M. Nanna, L. Ellingson & D. Tallman, "Aircraft Coatings Testing, Corrosion Sensors in Coatings and Mg-Rich Coatings as Cr-free Primers for Al 2024 T-3," Invited Presentation at 2002 AFOSR Corrosion Program Review to be held as part of the 2002 Tri-Service Corrosion Conference, Jan. 14-18, 2002, San Antonio, TX.

Gordon Bierwagen, Xianping Wang & Dennis Tallman, "In-Situ ENM and EIS Measurements by the Use of Imbedded Electrodes in Coating Films", Invited Presentation at UDRI Workshop on "Characterization of Corrosion Protective Coatings," December 3, 2001, University of Dayton, Dayton, OH.

Xianping Wang, Gordon P. Bierwagen, Stephen Mabbutt*, and Dennis E. Tallman, "SOME NON-CONVENTIONAL MEASUREMENT ELECTRODE CONFIGURATIONS FOR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND ELECTROCHEMICAL NOISE: MEASUREMENTS OF COATED METALS AND THEIR POSSIBLE USES," KEY NOTE LECTURE at Congress Proc. EuroCorr2001, European Corrosion Congress, Riva del Garda, Lake Garda, Italy, Sept 30th - Oct 4th 2001.

"Evaluation of Functionalized Polysiloxanes as Aircraft Coating Primers" ; Philip Boudjouk, Thomas E. Ready, and Seok-Bong Choi *2002 Tri-Service Corrosion Review*, San Antonio, TX; January 2002.

"Cerium Corrosion Inhibitor in Polysiloxane Primers" Thomas E. Ready and Philip Boudjouk *2002 Tri-Service Corrosion Review*, San Antonio, TX; January 2002.

S. G. Croll and A. D. Skaja, "Quantitative Use of Ultraviolet Spectroscopy To Calculate the Effective Irradiation Dosage During Weathering," to be presented at XXVI FATIPEC Congress, "Coatings and Pigments," September 9 - 11, 2002. Dresden, Germany.

b. *Consultative & Advisory Functions*

D. E. Tallman:

- Journal of Solid State Electrochemistry, Regional Editor for North America, 1997-present.
- Board of Directors, Society for Electroanalytical Chemistry (SEAC), 1998-2002.

Gordon Bierwagen:

- North Dakota State University Research Foundation, Board of Directors (1996-present)
- NDSU College of Science & Mathematics - Student Progress Committee, 1994-present
- Technical Advisory Board, Athens Annual Conferences on Science and Technology of Organic Coatings, Institute of Materials Science, New Paltz, NY, 2000 -present
- AFRL-Materials & Mfg. Lab-Scientific Advisory Review Board 2001-present
- Nanotechnology Planning Group for NDSU Center for Nanoscale Science and Technology
- EPA Reviewer Panel for SBIR Proposals on Nanomaterials & Clean Technology

c. *Transitions*

Year 1

Provisional Patent Pending (joint with University of Wollongong, Australia) – Catalytic electrodeposition of polypyrrole on aluminum alloy.

We anticipate two patents to result from our research. We have filed the following disclosures with North Dakota State University's Technology Transfer Office:

1-"A New Silicone Based Support for Hydrosilation Catalysts"

2-"A Catalytic Process for Attaching Bifunctional Ligands to Polysiloxanes"

We are currently negotiating commercialization of 1 with a U. S. based silicone manufacturer.

Year 2

We applied for a patent based on our research.

"Method of Preparing Aminofunctional Alkoxy Polysiloxanes"

U.S. Patent Application No. 09/771,921

We have filed the following disclosures with North Dakota State University's Technology Transfer Office:

1-"A New Silicone Based Support for Hydrosilation Catalysts"

2-"A Catalytic Process for Attaching Bifunctional Ligands to Polysiloxanes"

Year 3

D. E. Tallman: Provisional Patent (joint with University of Wollongong, Australia), "Catalytic electrodeposition of polypyrrole on aluminum alloy," (2002).

U.S. Patent Application 09/771,921 "Method of Preparing Aminofunctional Alkoxy Siloxane" (Filed Jan. 2001; Notification for issuance received July 2002) to NDSU; Co-inventors: Philip Boudjouk, Thomas E. Ready, Bhanu Chauhan.

International Patent Application PCT/US02/01225 "Antineoplastic Polyalkoxyalkyl Siloxanes and Methods of Use Thereof" (Filed Jan. 2001; Application published July 2002) to NDSU; Co-inventors: Philip Boudjouk, Thomas E. Ready, Shane Stafslie.

Part 5. Honors/Awards:

Dennis E. Tallman

Intelligent Polymer Research Institute Fellow, University of Wollongong, Australia, 2000.

Fred Waldron Award for Outstanding Research, NDSU Development Foundation, 2000.

Appointed Honorary Professor, North China Institute of Technology, October 2000 (lifetime appointment).